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Serial No.: 10/601,897

Docket No.: 32779

Remarks:

Claims 1-40 remain for consideration in this application. Claims 1, 9, 19, and 26 have been amended in response to the office action. Claim 8 has been amended to correct a minor typographical error (i.e., to amend "X" to read "X¹"). It is believed this correction would easily be identified by one reading the specification or the claims. Finally, claims 33-40 are newly added and discussed in more detail below.

Turning now to the office action, the Applicants note with gratitude that claims 9-18 and 26-32 have been allowed. Of the remaining claims, claims 1 and 19 were rejected, and claims 2-8 and 20-25 were objected to as depending from rejected claims.

In the sole rejection, the Examiner rejected claims 1 and 19 as being based upon a non-enabling disclosure under 35 U.S.C. § 112, first paragraph. The Examiner stated that claims 1 and 19 do not show where the chromophores bind to the metal, which is essential to the practice of the invention.

First, the Applicants believe the Examiner raised the rejection against these two claims because X is not drawn with a binding site shown. Thus, the drawings showing the possible structures for X have been amended to designate respective binding sites (*) on each structure. The two structures that have been deleted are so designated by the use of brackets around the deleted material, which the Applicants believe to be appropriate under the current claim amendment format rules. Of course, the newly added material has been underlined.

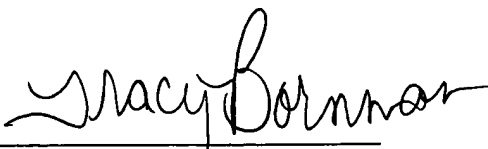
It is respectfully submitted that one of ordinary skill in the art would know from a reading of the present disclosure that the chromophore binds to the metal atom (M) through the R² or R³

group, and that these amendments are, therefore, supported by the specification as filed. This occurs through a ligand exchange or substitution process, which is known in the art and is described in Exhibit A. F. Albert Cotton et al. *Basic Inorganic Chemistry*, 187-191 (3d ed. 1995). A ligand bonded to the metal center of the complex is replaced by another ligand dissolved in solution. This reaction proceeds through either an associative or dissociative mechanism, with both mechanisms having the same result. This reaction is an equilibrium process, and occurs at ambient conditions, as described in Examples 2 and 3 of the specification. One of ordinary skill in the art would readily understand the way in which the chromophore binds to the metal center; thus this disclosure is enabling, and this rejection has been overcome.

Each of the independent claims has further been amended to add a third structural formula for X. This structure is directed towards the embodiment found in Example 2 (Structure A) on page 9, lines 17 et seq. of the application, with the variables taught for this structure on page 4, lines 1-6 and 13-19 of the application. New claims 33-40 have been added to more specifically focus on this preferred embodiment.

It is believed that no further issues should exist with the present application, and that a Notice of Allowance is in order. However, if further issues remain, the Examiner is urged to contact the undersigned at 800-445-3460 to resolve this issues and expedite prosecution of this application. Any additional fee due in conjunction with this amendment should be applied against our Deposit Account No. 19-522.

Respectfully submitted,

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EXHIBIT

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It is evident that both enthalpy and entropy favor the chelate complex, but the entropy contribution is far more important. Data for a large number of these reactions, with many different metal ions and ligands, show that enthalpy contributions to the chelate effect are sometimes favorable, sometimes unfavorable, but always relatively small. The general conclusion is that *the chelate effect is essentially an entropy effect*. The reason for this is as follows.

The nickel ion is coordinated by six H_2O molecules. In each of the first two reactions, these six H_2O molecules are liberated when the nitrogen ligands become coordinated. On that score, the two processes are equivalent. However, in one case *six* NH_3 molecules *lose* their freedom at the same time, and there is no net change in the number of particles. In the other case, only *three* *en* molecules lose their freedom, and thus there is a net increase of 3 mol of individual molecules. The reaction with three *en* causes a much greater increase in disorder than does that with six NH_3 molecules and, therefore, ΔS° is more positive (more favorable) in the former case than in the latter. It is easy to see that this reasoning is general for all such comparisons of a chelate with a nonchelate process.

Another way to state the matter is to visualize a chelate ligand with one donor atom attached to a metal ion. The other donor atom cannot then get very far away, and the probability of it, too, becoming attached is greater than if it were in an entirely independent molecule, with access to the entire volume of solution. Thus the chelate effect weakens as ring size increases. The effect is greatest for five- and six-membered rings, becomes marginal for seven-membered rings, and is unimportant thereafter. When the ring to be formed is large, the probability of the second donor atom attaching itself promptly to the same metal atom is no longer large as compared with its encountering a different metal atom, or as compared with the dissociation of the first donor atom before the second one makes contact.

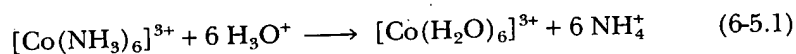
6-5 Reactivity of Coordination Compounds

Virtually all of transition metal chemistry and a great deal of the rest of inorganic chemistry could be included under this title, taken in its broadest sense. Only three aspects will be covered in this and the following sections: substitution, electron-transfer, and isomerization reactions. Additional aspects of reactivity will be discussed in Chapters 28–30, under organometallic compounds. A detailed correlation of structure, bonding, and reactivity will have to be postponed until Chapter 23 and later, when a discussion of bonding in coordination compounds can be developed.

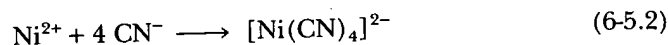
Substitution Reactions of Octahedral Complexes

The ability of a complex to engage in reactions that result in replacing one or more ligands in its coordination sphere (by other ligands in solution, for instance) is called its lability. Those complexes for which such substitution reactions are rapid are called **labile**, whereas those for which such substitution reactions proceed slowly (or not at all) are called **inert**. We note that these terms are kinetic terms, because they reflect rates of reaction. These terms should not be confused with the thermodynamic terms **stable** and **unstable**, which refer to the tendency of species to exist (as governed by the equilibrium constants K or β)

under equilibrium conditions. A simple example of this distinction is provided by the $[\text{Co}(\text{NH}_3)_6]^{3+}$ ion, which will persist for months in an acid medium because of its kinetic inertness (slow reactivity) despite the fact that it is thermodynamically unstable, as shown by the large equilibrium constant ($K \sim 10^{25}$) for Reaction 6-5.1.



In contrast, the overall formation constant ($\beta_4 = 10^{22}$) for Reaction 6-5.2 indicates that the thermodynamic stability of $[\text{Ni}(\text{CN})_4]^{2-}$ is high.

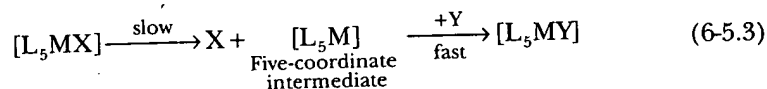


Nevertheless, the rate of exchange of CN^- ligands with excess CN^- in solution is immeasurably fast by ordinary techniques. The complex $[\text{Ni}(\text{CN})_4]^{2-}$ is both thermodynamically stable and kinetically labile; the terms are not contradictory. In other words, it is not required that there be any relationship between thermodynamic stability and kinetic lability. Of course this lack of any necessary relation between thermodynamics and kinetics is generally found in chemistry, but its appreciation here is especially important.

A practical definition of the terms labile and inert can be given. Inert complexes are those whose substitution reactions have half-lives longer than a minute. Such reactions are slow enough to be studied by classical techniques where the reagents are mixed and changes in absorbance, pH, gas evolution, and so on, are followed directly by the observer. Data can be taken conveniently for such reactions. Labile complexes are those that have half-lives for a reaction under a minute. Special techniques are required for collecting data during such reactions, as they may appear to be finished within the time of mixing.

In the first transition series, virtually all octahedral complexes save those of Cr^{III} and Co^{III} , and sometimes Fe^{II} , are normally labile; that is, ordinary complexes come to equilibrium with additional ligands (including water) so rapidly that the reactions appear instantaneous by ordinary techniques of kinetic measurement. Complexes of Co^{III} and Cr^{III} ordinarily undergo substitution reactions with half-lives of hours, days, or even weeks at 25 °C.

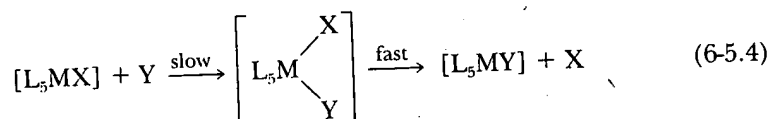
Two extreme mechanistic possibilities may be considered for any ligand substitution process or for any single step in a series of substitution reactions. First, there is the dissociative (D) mechanism in which the ligand to be replaced dissociates from the metal center and the vacancy in the coordination sphere is taken by the new ligand. This mechanism is shown in Reaction 6-5.3:



where L represents a nonlabile ligand, X is the leaving ligand, and Y is the entering ligand. The important feature of such a mechanism is that the first step (dissociation of the leaving group) is rate determining. Once formed by cleavage of the bond to the leaving group, X, the five-coordinate intermediate will react with the new ligand, Y, almost immediately. This mechanism for ligand substitution is comparable to the $\text{S}_{\text{N}}1$ mechanism in organic systems, because the

formation of the intermediate with reduced coordination number is unimolecular, as well as rate determining.

The other extreme possibility for ligand substitution is the addition-elimination mechanism, or the associative (A) mechanism. In this case the new ligand, Y, directly attacks the original complex to form a seven-coordinate intermediate in the rate-determining step, as shown in Reaction 6-5.4.

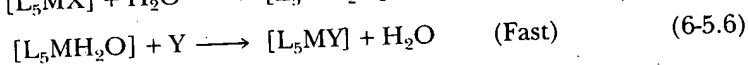
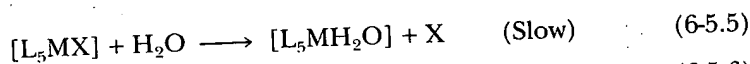


After rate-determining association between the entering ligand Y and the metal complex, the leaving group X is lost in a fast step. The rate-determining step is bimolecular for the mechanism shown by Reaction 6-5.4.

Unfortunately, these two extreme mechanisms are just that—extremes—and observed mechanisms are seldom so simple. Instead of a five- or seven-coordinate intermediate, a transition state may be reached in which some degree of bond breaking accompanies a given degree of bond making. The interchange of the ligands X and Y could be accomplished mostly by breaking the bond to the leaving group (interchange-dissociative, I_d) or by making the bond to the entering group (interchange-associative, I_a), but in each case both ligands are bound to the metal to one extent or another. Figure 6-5 presents reaction profiles for each of the four mechanistic cases just mentioned.

To complicate matters further, the rate law that is determined for a reaction from kinetic data cannot be used to identify the mechanism for that reaction. This is so because additional steps in the overall substitution may take place, obscuring the simple first- and second-order rate laws that are expected for unimolecular and bimolecular processes, respectively. The three most important cases that illustrate this sort of complication are (1) solvent intervention, (2) ion-pair formation, and (3) conjugate-base formation.

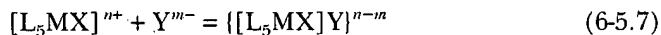
1. Solvent intervention. Many reactions of complexes have been studied in solvents that are themselves ligands. Water, for instance, is a respectable ligand, and is present in aqueous solution in high and effectively constant concentration ($\sim 55.5\text{ M}$). The substitution of X by Y might take place by the sequence of Reactions 6-5.5 and 6-5.6.



A simple first-order rate law would be observed, and yet either Reaction 6-5.5 or 6-5.6 could proceed by an A (or I_a) or a D (or I_d) mechanism.

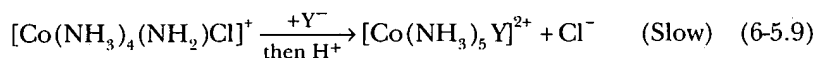
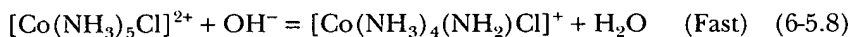
Intervention of the solvent in Reaction 6-5.5 obscures the molecularity of the rate-determining step; the reaction will necessarily be observed to be first order because of the high and constant concentration of the entering ligand, H_2O .

2. Ion-pair formation. When the reacting complex and the entering ligand are both ions, especially when both have high charges, ion pairs (or outer-sphere complexes, as they are sometimes called) will form, as in Reaction 6-5.7.



In the product of Reaction 6-5.7, the entering ligand Y has been stabilized at the outer edge of the coordination sphere of the complex $[L_5MX]^{n+}$ primarily by electrostatics. In cases where charges on ions are not involved, an entering group Y may be bound at the periphery of the metal complex through, for instance, hydrogen bonding. Outer-sphere or ion-pair equilibrium constants K_{os} are generally in the range 0.05–40, depending on the charges on the ions and on their effective radii. Where ion pairs (or neutral outer-sphere complexes) are featured as intermediates in the reaction path that leads to ligand substitution, then observed rate laws will be second order, whether or not the mechanism at the rate-determining step involves associative or dissociative activation.

3. Conjugate-base formation. When experimental rate laws contain $[OH^-]$, there is the question whether OH^- actually attacks the metal in a true associative fashion, or whether it appears in the rate law through operation of the mechanism shown in Eqs. 6-5.8 and 6-5.9.



In this conjugate-base (CB) mechanism, the hydroxide first deprotonates a ligand (usually NH_3) forming the conjugate base, here leading to the NH_2^- ligand. It is then the conjugate base of the original metal complex that reacts with the incoming ligand, as in Eq. 6-5.9.

Water Exchange in Aqua Ions

Since many reactions in which complexes are formed occur in aqueous solution, one of the most fundamental reactions to be studied and understood is that in which the water ligands in the aqua ion $[M(H_2O)_n]^{m+}$ are displaced from the first coordination shell by other ligands. Included here is the simple case in which the new ligand is another water molecule, the water-exchange reaction.

A partial survey of results is given in Fig. 6-6. Not shown here are systems where the water exchange is characteristically slow: Cr^{3+} , Co^{3+} , Rh^{3+} , Ir^{3+} , and Pt^{2+} . These five typically inert aqua ions have exchange rate constants in the range 10^{-3} – $10^{-6} s^{-1}$. Those ions included in Fig. 6-6 are broadly considered to be

Figure 6-5 The four general mechanisms for ligand substitution in the complexes $[ML_5X]$, where L are nonlabile ligands, X is the leaving ligand, and Y is the entering ligand. (a) The associative (A) mechanism in which an intermediate of expanded coordination number is formed first through rate-determining entry of the ligand Y. (b) The interchange-associative mechanism (I_a), in which the transition state is reached mostly through formation of the bond ($M \cdots Y$) to the entering ligand. The notations $[ML_5X];Y$ and $[ML_5Y];X$ for the reactants and products, respectively, represent outer-sphere complexes (or ion pairs) as formed in Reaction 6-5.7. (c) The interchange-dissociative mechanism (I_d), in which the transition state is reached mostly through breaking the bond ($M \cdots X$) to the leaving ligand. Again, the reactants and products are outer-sphere complexes (or ion pairs) as featured in Reaction 6-5.7. (d) The dissociative or D mechanism in which an intermediate of reduced coordination number is formed first through rate-determining cleavage of the bond to the leaving group.

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